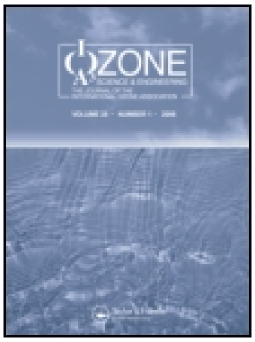

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Ozone Treatment Of Cooling Water: Results Of A Full-Scale Performance Evaluation

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Abstract

This paper is the first technical status report of a continuing evaluation of ozone treatment for cooling tower water. Data will be presented that illustrate the results of ozone treatment in a 3,400-ton air-conditioning cooling system at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, which is operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.[1] Heat transfer data and equipment inspections confirm that a threshold surface temperature exists, below which heat exchange surfaces remain free of mineral scale. Heat exchange surfaces that exceed the temperature threshold experience calcium carbonate scaling. The temperature threshold effect may explain why ozone treatment has been reported as a successful treatment for air conditioning cooling towers, but has not been successful in higher temperature process cooling systems. Plans for future ozone investigations will be discussed.

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[1] The Oak Ridge Y-12 Plant, located at Oak Ridge, Tennessee, is operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

Introduction

The 20 cooling towers at the Oak Ridge Y-12 Plant have a total system volume of 1.5 million gallons of water, servicing over 40,000 tons of air-conditioning-refrigeration load. The cooling tower structures include both crossflow and counterflow design from a variety of cooling tower manufacturers.

From 1974 through 1984, the Y-12 Plant used all-organic chemicals for the water treatment program for the cooling towers. Prior to 1974, all of the cooling towers were treated with a chromate/zinc corrosion inhibitor with pH control and sodium pentachlorophenate microbiocide. The Y-12 Plant has used many different chemical vendors in the past. Additional extensive studies of various water treatment programs have been conducted to satisfy more recent regulatory guidelines. This report reviews what has been completed to date in the development of one of the Y-12 Plant's alternatives.

Background

In 1975 the Y-12 Plant was issued a National Pollutant Discharge Elimination System (NPDES) permit from the U.S. Environmental Protection Agency (EPA) and the State of Tennessee, Department of Health and Environment, as required by the Clean Water Act. The NPDES permit consolidated essentially all of the Y-12 Plant's wastewater discharges into a single discharge point. All 20 cooling towers discharge their blowdown into Upper East Fork Poplar Creek, which flows through a settling pond and is discharged through the single NPDES point at the outfall of the pond. The cooling tower blowdown makes up ~10% of the total flow discharged. None of the NPDES parameters directly affected the cooling tower blowdown with the use of the all-organic treatment program.

In 1983 the State of Tennessee and EPA began revising the Y-12 Plant's NPDES permit. They began to permit point sources that discharged to Upper East Fork Poplar Creek above the settling pond. The single discharge point became 290 discharge points, and the permit directly addressed cooling tower blowdown water. The following parameters were addressed in the permit with regard to cooling tower water: toxicity, pH, temperature, free and total chlorine, chromium, zinc, and other physical parameters. Late in 1983 the cooling tower water treatment program was checked against the above criteria (using the acute fathead minnow test) and found to be toxic. A rigorous search was initiated to find "non-toxic" treatment programs that could be implemented in all of the cooling towers that met the criteria of the proposed NPDES permit in the spring of 1985.

At this time, there was an increasing awareness of concerns with *Legionella* bacteria in cooling tower waters. Dr. R.L. Tyndall, a microbiologist with the Oak Ridge National Laboratory, has monitored the *Legionella* bacteria counts in U.S. Department of Energy facilities since 1979 and has shown much interest in the microbiocides that have been used at the Y-12 Plant (1). Dr. Tyndall has a strong interest in the effects of ozone treatment on *Legionella* and suggested its use as a microbiocide (2). After literature searches and discussions with vendors and other ozone users, it was noted that ozone may do more than act as a microbiocide. It was reported in the literature that ozone is the only treatment necessary for microbiological, corrosion, and deposition control (3-5). Another major benefit reported was that the discharge of a blowdown stream from an ozone treated tower was not necessary to prevent scaling. If there were no discharges, the criteria for the NPDES permit regarding cooling towers would be of no consequence.

After the review of ozone for cooling tower water use was completed, the Utilities Department decided to conduct a trial demonstration to show how well ozone would perform at the Y-12 Plant. When funding for such an extensive undertaking became available, a statement of work was developed and a local engineering firm with knowledge of cooling towers and water treatment was contracted to perform the study on a "turn-key" basis. The engineering firm was Environmental Systems Corporation (ESC) of Knoxville, Tennessee.

Objectives

The main objective of the study was simple -- compare the effectiveness of ozone with the effectiveness of the conventional chemical treatment it would replace, if successful. The objective may have been simple, but the work to be accomplished was quite extensive. The study was to prove or disprove the results obtained in other similar studies and completely reconcile the uncertainty of ozone technology use for the Y-12 Plant. Furthermore, in conducting such a study, it was believed the results could be biased unless a third-party investigator was used, one that did not market cooling tower water treatment chemicals or ozone equipment. ESC met this requirement.

Prior studies documented ozone treatment results observed in small (< 600-ton) cooling tower systems. A full-scale, rather than pilot-scale, study in one of the larger systems at the Y-12 Plant was preferred. The study was performed on a system designed for 5,000 tons of refrigeration.

The Y-12 Plant study had to be performed in the summer months in order to have full-load condition on the cooling tower. Because loads in fall, winter, or spring are low and erratic, consistency would be a problem during these times. In accomplishing the objectives of the study, emphasis was placed on the following areas:

- microbiological,
- corrosion,
- deposition,
- heat-exchange efficiency,
- cooling tower efficiency, and costs.

Procedures were developed to address the above parameters, and a study plan was formulated and aggressively pursued. Design work for the ozone delivery and monitoring systems began immediately after the selection of the test cooling tower. The main criterion, which was used to select the test tower, was that it must be representative of all the other cooling tower systems at the Y-12 Plant.

System Description

COOLING TOWER SYSTEM

The cooling tower system selected (Cooling Tower 9409-2) at the Y-12 Plant consists of three cross-flow mechanical draft cooling towers situated over a common cold-water basin (Figure 1). The three towers have a total of five cells. Three of the cells are equipped with cross-flow film fill fabricated from polyvinyl chloride (PVC) sheets, and the other two cells contain PVC splash packing oriented perpendicular to the airflow. At maximum heat load, the recirculation rate would be 15,000 gal/min (56,800 L/min) with approximately 3,000 gal/min (11,350 L/min) distributed over each cell. The cold water from the basin serves 3,400 tons of installed refrigeration chillers and the intercoolers and aftercoolers of two air compressors. The 3,400 tons of refrigeration consists of two 1,000-ton Trane, a 1,000-ton Westinghouse, and a 400-ton Worthington vapor-compression chillers.

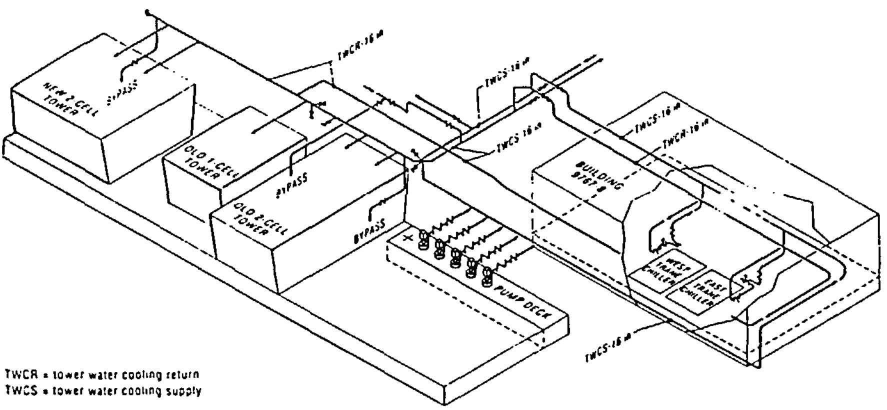

Figure 1. Isometric diagram -- cooling tower water system.

To evaluate the effectiveness of ozone gas as a stand-alone treatment for circulating cooling water at the Y-12 Plant, it was necessary to install facilities for the delivery of ozone into the Cooling Tower 9409-2 cooling water circuit and facilities to monitor the results of treatment.

OZONE SYSTEM

Since ozone is a very reactive molecule, it was necessary to build a system that would generate the required amount of ozone and then immediately effect the transfer of the ozone into a side-stream of the Cooling Tower 9409-2 circulating water loop. This on-site ozone delivery system consisted of a conventional "corona discharge" ozone generator of 21 lb/d (400 g/h) capacity and a "contactor" of the static-mixer type.

In the ozone generator, an air stream of ca 10 scfm (280 L/min) flow rate and -60°F (-51°C) dew point was exposed to a high-voltage corona discharge of variable frequency. The air stream leaving the ozone generator contained up to 2.0 vol % ozone (O_3). The ozone-laden air was conveyed to the inlet end of the static-mixing contactor, where it was sparged into a cooling water side-stream of ca 1,000 gal/min (3,852 L/min) flow rate.

In the contactor, the water stream and the ozone-air stream were mixed intimately by the fluid shear induced by the mixing vanes. From the outlet of the contactor, the air and water flowed in two mixed, but separate, phases to multiple injection points below the water surface in the cold-water basin of Cooling Tower 9409-2. Disengaging of the ozone-depleted air and ozone-enriched water occurred in the cold-water basin. The injection pipes were grouped into pairs near the suction inlets of each of the five circulating water pumps. Also, individual injection pipes were located in each of the four corners of the cold-water basin. Figure 2 is a schematic diagram of the ozone delivery system.

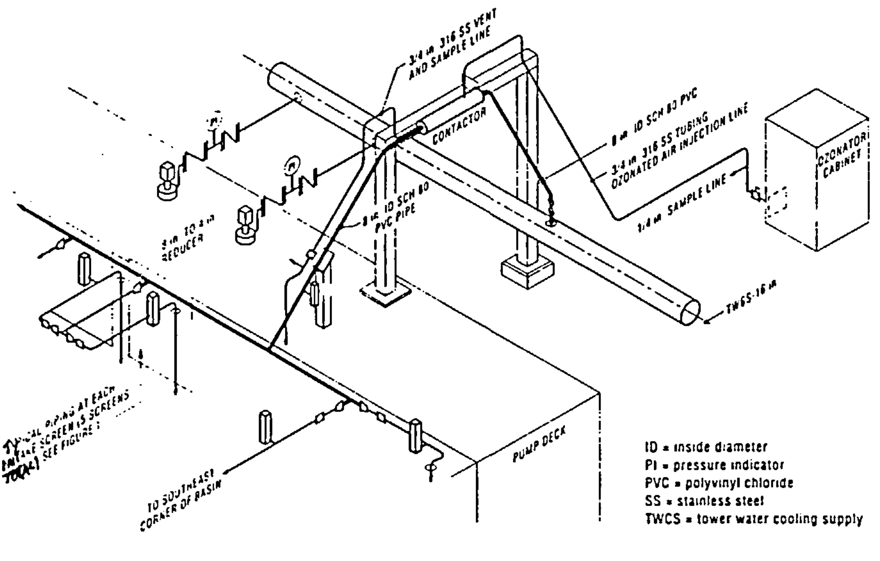

Figure 2. Isometric diagram -- ozone injection piping.

PERFORMANCE MONITORING SYSTEM

The performance monitoring system was custom designed to provide a continuous data base of highly accurate temperature, pressure, flow rate, corrosion rate, fouling rate and water chemistry data for use in evaluating the success of the stand-alone ozone treatment program. The system consisted of a Precision Temperature Scanner (PTS-80B), a remote data logger (AQM-8000), an array of sensors and analyzers, and a central processor (personal computer) that communicated with the logger by telephone modems. Figure 3 presents a schematic diagram of the system and its interconnections. Each major role of the monitoring system is described in the following paragraphs.

The temperature, pressure, and flow rate data continuously logged by the monitoring system were used for two main purposes during the study. On a daily basis, the data were reviewed for any indications that the operating conditions of the cooling system or the ozone delivery system had changed. The data also were used as an indication of fouling in the condenser tubes of one of the 1,000-ton Trane vapor-compression chillers. Any increases in condensing pressure vs heat load were indicative of fouling on the water side of the condenser or accumulation of noncondensible gases on the vapor side. Inspection of the condenser and/or operation of the vacuum pump were sufficient to verify which factor caused the high condensing pressure. A differential pressure (DP) transmitter, connected across the water side of the condenser, was used as an indicator of fouling in the condenser tubes.

Corrosion rates for copper and carbon steel were monitored continuously using twin-element linear polarization instruments connected into the data logger network. The corrosion rate readings from these instruments were compared with rates determined by coupon weight-loss analysis.

The pH and redox-potential instruments were used as indicators of proper operation of the ozone delivery system. If the redox-potential reading was in the range of 750 to 850 mV, the ozone system was delivering ozone at or near its rated capacity. If the reading was in the range of 400 to 750 mV, something was wrong with the ozone delivery system. Also, a check of the output data, from an ozone analyzer on the air stream leaving the ozone generator, showed at a glance if the generator was operating properly.

Two monitoring devices that were very important to the study were not connected into the data-logger network. These were the Scalometer™ and the Biofouling Monitor (6). Both of these devices were used to monitor fouling on water-wetted surfaces. The Scalometer™ (Rohrback Cosasco Systems, Inc.) employed a heated element, set to a preselected surface temperature, and a unique thermal bridge technique to monitor fouling by minerals exhibiting retrograde solubility with temperature (7). The Biofouling Monitor consisted of an unheated pressure drop tube with a DP indicator for long-term tracking of the frictional resistance to flow caused by a biological film in the tube. The purpose of the Scalometer™ was to simulate the operating conditions in high-temperature heat exchangers, while the purpose of the Biofouling Monitor was to simulate conditions in the low-temperature heat exchangers and piping systems of the cooling water circuit.

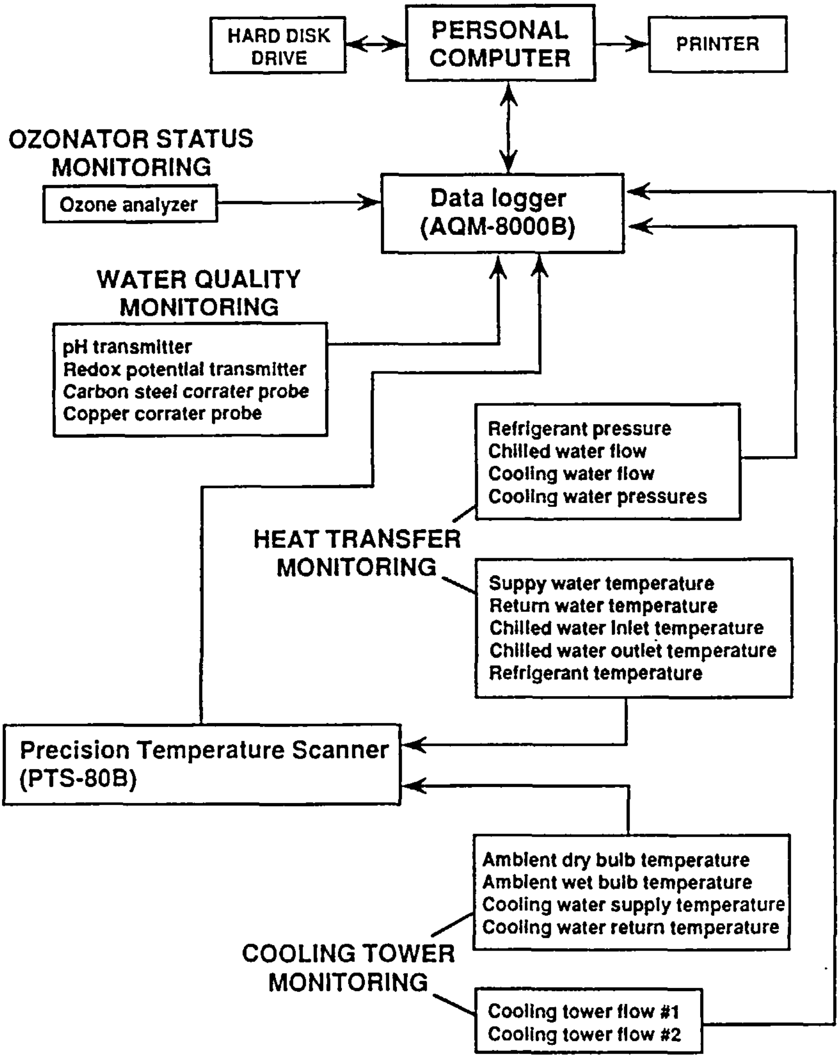

Figure 3. Data flow diagram of the Y-12 Plant performance monitoring system.

In addition to the continuous stream of data from the performance monitoring system, supplemental investigations were conducted using standard laboratory techniques (8). The main goal of these investigations was to document the chemical and biological equilibria associated with the use of ozone as a stand-alone treatment for Y-12 Plant cooling water.

Methods And Results Of Investigation

WATER CHEMISTRY INVESTIGATIONS

The primary chemical parameters of interest were the free ozone residual, the stability indices for calcium carbonate solubility, and the individual concentration ratios of the following mineral species:

- calcium ion,
- magnesium ion,
- chloride ion, and
- sodium ion.

DETERMINATION OF FREE OZONE RESIDUAL

The method used during the study for determining the free ozone residual concentration in water was the spectrophotometric method employing potassium indigo-trisulfonate as an indicator and absorbance measurements at a wave length of 600 nm (9). This method is highly specific for ozone and is sensitive to ozone concentrations as low as 0.01 mg/L. Grab samples of circulating cooling water were collected from various locations in the cooling water circuit and immediately analyzed by the indigo method.

Table 1 shows a concentration profile of ozone residual at steady state conditions and maximum capacity on the ozone generator. At a generation rate of 22.8 lb/d (435 g/h), the injection water leaving the contactor had an ozone concentration of 0.95 mg/L. By the time that the water had been injected into the cold-water basin and traveled to the pump discharge, the ozone residual had dropped to 0.092 mg/L. The concentration of ozone stayed at this level into the inlet of the chillers. Hot water leaving the chillers had an ozone concentration of 0.086 mg/L, and the hot water entering the distribution basins at the top of the cooling tower had a concentration of 0.081 mg/L. By the time the water had fallen through the fill section of the tower, the ozone residual concentration was below the detection limits of the indigo method.

Table 2 shows some interesting facts about the relationship between ozone supply and demand for the cooling water. Of the 0.957 lb/h (7.25 g/min) of ozone produced in the ozone generator, only 4% failed to be transferred from the air phase to the water phase in the contactor. Of the 96% that did transfer to the water phase, 39% decomposed in the injection water piping manifold, and another 45% decomposed immediately after injection into the cold-water basin. After this immediate demand (totaling 88% of the generated ozone) was satisfied, the ozone residual persisted through the chiller condensers and all the way back to the cooling tower. Only 1% of the generated ozone decomposed in the piping loop between the pump discharge and the hot-water basins of the cooling tower. The remaining 11% of the ozone was air stripped out of the cooling water as it fell through the fill section of the tower.

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TABLE 1. OZONE CONCENTRATION IN COOLING TOWER WATER SYSTEM

Location	Concentration mg/L	Flow L/min
Injection water feed	0.95	4,825
Pump discharge	0.092	10,000
Chiller outlet	0.086	
Cooling tower hot-water basin	0.081	
Fill discharge	0.00	
Basin water	0.00	
NOTE: To convert L/min to gal/min, multiply by 0.264.		

TABLE 2. OZONE INVENTORY

Position	Rate - g/min	Percentage
Ozone production	7.25	100
Offgas	0.30	4
Absorbed in contactor	0.95	96
Decomposed in contactor	2.82	39
Decomposed at injector	3.24	45
Decomposed in chiller loop	0.10	1
Removed in fill	0.81	11
NOTE: To convert g/min to lb/h, multiply by 0.132.		

The 0.092-mg/L ozone residual concentration, corresponding to the persistent 12% of the generated ozone, was sufficient to raise the redox potential of the cooling water from the range of 350 to 450 mV to the range of 750 to 850 mV. The relatively wide range of redox potential encountered in the cooling water before the start of ozone treatment was attributable to the residual chlorine entering the system in the makeup water. The redox potential would rise to the upper end of the range whenever the makeup water valve opened.

Figure 4 shows a decomposition curve for ozone in the cooling water. The half-life for ozone in this water system was 8.75 min.

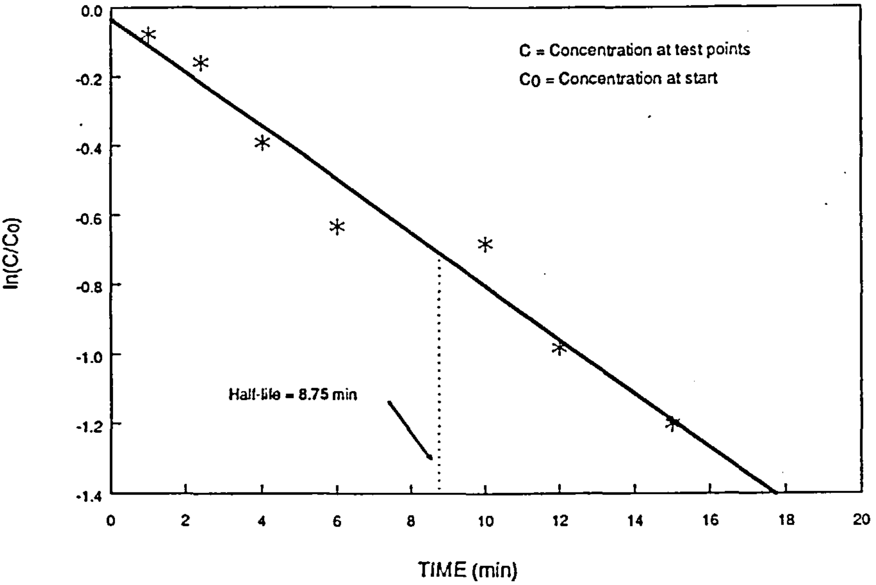

Figure 4. Decomposition rate of ozone in tower water.

DETERMINATION OF STABILITY

Grab samples of circulating water from the cooling system were collected roughly three times per week throughout the ozone evaluation study. Makeup water samples were collected once per month. These samples were analyzed in the laboratory at the Y-12 Plant for a variety of chemical parameters. Table 3 shows typical analysis results.

Ryznar stability index was calculated as a check of the tendency toward calcium carbonate precipitation (10). Ryznar index, based upon water temperature, varied between 4.79 and 5.67. When based upon the metal surface temperatures, the Ryznar index varied between 3.69 and 4.53. As a review, recall that the neutral point of the Ryznar index is 6.0. Values below 6.0 are indicative of a tendency toward calcium carbonate precipitation. The greater the difference between the calculated value and the neutral point, the greater the tendency toward precipitation. The calculated Ryznar index values confirmed that the cooling water was in the precipitation range throughout the study. Furthermore, the severity of the imbalance was greatest at the heat exchange surfaces. Table 4 cross-references the concentration ratio with the Ryznar stability index for specific operational windows from the test program.

The tendency toward calcium carbonate precipitation was verified by two other methods during the study. The first was by visual observation; and the second was by comparison of the calculated concentration ratios based on the analyses of calcium, magnesium, and chloride. Table 4 shows the concentration ratios for these three parameters between September 1, 1987, and November 17, 1987.

TABLE 3. TYPICAL WATER ANALYSIS RESULTS (mg/L)[a]

Parameter	Makeup Water	Cooling Water: Pre-O_3 Injection	Cooling Water: During O_3 Injection
Cations			
Total Hardness (as $CaCO_3$)	130.6	509.8	497.9
Calcium (as $CaCO_3$)	91.3	347.5	320.0
Magnesium (as $CaCO_3$)	38.3	162.3	177.9
Sodium	4.4	24.0	21.3
Potassium	1.5	10.3	5.6
Manganese	< 0.002	0.020	< 0.001
Zinc	0.085	0.122	0.066
Iron	0.02	0.07	0.03
Copper	0.012	0.058	0.024
Anions			
Alkalinity (as $CaCO_3$)			
M	98	380	340
P	0	39	31
Chloride	8.3	43	43
Free Chlorine Residual	2.3	n/a[b]	n/a
Sulfate	26	108	110
Phosphorus (as P) Poly	0.36	1.3	0.60
Phosphorus (as P) Ortho	0.02	0.21	0.20
Solids			
Suspended	8	n/a	n/a
Dissolved	204	650	700
Volatile	40	n/a	n/a
Other			
Specific Conductance µmhos/cm)	311	950	950
Total Organic Carbon	1	n/a	n/a
pH	7.2	8.9	8.9

a Units given in mg/L unless specified otherwise or in the case of pH. b n/a = not applicable

TABLE 4. CONCENTRATION RATIOS BY PARAMETER

Date	Calcium	Magnesium	Chloride	Calcium as a % of chloride
09/01/87	3.93	4.17	4.22	93.1
09/15/87	4.34	5.13	4.82	90.0
09/20/87	3.22	4.25	4.33	74.4
09/22/87	3.47	4.65		
09/30/87	3.23	4.26	4.33	74.6
10/06/87	3.28	3.99	4.09	80.2
10/14/87	2.97	3.82	3.85	77.1
10/20/87	3.12	4.25	4.33	72.1
10/27/87	3.12	4.46	4.22	73.9
11/03/87	3.06	4.39	4.22	72.5
11/10/87	3.31	4.59	4.58	72.2

The concentration ratios based on chloride and magnesium were quite consistent in the range of 4.17 to 5.13. Sodium data proved too erratic to provide reliable concentration ratios. Despite the fact that the conductivity-controlled blowdown valve never opened during the entire study, the true concentration ratio was limited to the previously mentioned range by uncontrolled losses of circulating water. The concentration ratio, based on calcium in Table 4, ranged between 2.97 and 4.34 (77.1% and 90.0% of the concentration ratio based on chloride).

As previously stated, there was also visual evidence of calcium carbonate precipitation. Mineral scale was observed in three locations in the cooling tower system. While the study was still under way, scale was observed to form as an encrusting deposit of crystalline material on the surfaces of the film fill in two cells of the cooling tower. Also, a layer of these crystals resembling coarse sand accumulated on the floor of the cold-water basin directly beneath the bays of film fill. The cells of the cooling tower that had splash fill showed no evidence of scale encrustations or of the sandy material on the basin floor beneath the splash fill bays.

At the conclusion of the study, some of the small-diameter carbon steel pipes feeding cooling water into the on-line analyzers were dismantled and inspected. In all of these lines, a thin white powdery film was found. The film appeared to be slightly thicker in the lines carrying hot water from the outlet of the chillers than in the lines carrying cold cooling water. Since these lines were installed specifically for the ozone study, the deposits could not have resulted from the previous water treatment program.

The other location where scale was observed was in an air compressor intercooler served by the cooling system. The average tube surface temperature of this heat exchanger was in excess of 160°F (71°C). A hard, thin layer of grey-brown scale was found on the tubes of this exchanger when it was inspected at the conclusion of the study. Since it was not inspected prior to the start of ozonation, there is no way to be certain if this scale occurred during the ozone study. However, the Scalometer™ operation revealed a strong tendency toward scale for heat-transfer surface temperatures exceeding 130 to 135°F (54 to 57°C). The Scalometer™ investigations are presented in detail in the Special Investigations section of this paper.

All other locations within the cooling water circulation system remained completely free of mineral scale. This was conspicuously true of the copper tubes in the chiller condensers. This subject will be presented in detail in the section on Special Investigations.

MICROBIOLOGICAL INVESTIGATIONS

Throughout the ozone evaluation study, grab samples of circulating cooling water were collected in sterile plastic bags and analyzed by a contract laboratory for important microbiological indicators. The frequency of sampling was approximately twice per week. Each sample was diluted as necessary with sterile dilution water and subjected to standard plate count analysis. Also, an attempt was made to grow sulfate-reducing bacteria from the samples, but these attempts were largely unsuccessful.

A method was developed for the microscopic detection of algae in the samples. After the aliquots were removed and inoculated into the media for the plate count and sulfate reducing bacteria analyses, the remaining sample was centrifuged to concentrate the large microorganisms at the bottom of the centrifuge tubes. A pipette then was used to draw a sample of the centrifugate and make a hanging drop wet mount for viewing under the microscope. By this method, any algae present in the original sample would be seen.

The results of the microbiological investigation revealed that continuous ozone treatment produced a thousand-fold reduction in total bacteria in the circulating water. Total plate count values dropped from the ten-thousands of colony forming units (CFU) per milliliter to the tens per milliliter. Although the incremental reduction in plate count seems very dramatic, the preozonation plate counts were actually quite low by comparison with the millions of CFU per milliliter that are commonly found in industrial cooling towers (10-12). The sulfate-reducing bacteria were nondetectable in the cooling water samples, both before and after the start of ozone treatment. Algae, which were present in the cooling water prior to the start of ozone treatment, disappeared after the start of ozonation. Visual observation of the cooling tower fill and hot- and cold-water basins supported the conclusion that algae had been virtually eliminated. Prior to ozonation, the water in the cold-water basin had a turbid green coloring. Within one week after the start of ozone treatment, the water in the cold-water basin appeared clear, with no color and a very low turbidity. Algae that had been growing on the corrugated end walls of the cooling tower cells largely disappeared. The only places where algae remained were locations that were not effectively contacted by the circulating water.

Dr. Tyndall's search for *Legionella* in samples of the ozonated cooling water produced negative results. However, this is inconclusive because no *Legionella* was found in the cooling water before ozonation began.

DETERMINATION OF CHARACTERISTIC CORROSION RATES

During the ozone treatment evaluation, corrosion rates were monitored by instrumental methods and by coupon weight-loss analysis. The two metals investigated were copper (condenser tube material) and carbon steel (piping material). Early in the study, the copper corrater probe developed a short that resulted in this instrument being dropped from the study plan. The carbon steel corrater probe remained in service throughout the study and provided a point of comparison for the coupon data.

Table 5 shows a summary of the corrosion data collected during the ozone study. The corrater readings, the coupon data, the typical Ryznar index values, and the concentration ratios are compared. Note that the corrater readings of the carbon steel probe were roughly two to six times higher than the values determined by coupon weight loss. This offset is not unusual for the two-element linear polarization probes employed during the study (13). The corrater data were used primarily for trend analysis. The coupon data show that the equilibrium corrosion rates for carbon steel are as good as those provided by conventional alkaline water treatment programs. However, the copper corrosion rates of 0.1 to 0.2 mil/year appear to be somewhat higher than those expected from a conventional treatment program.

TABLE 5. CORROSION RATE DATA

Time period (1987)	Corrater reading (mils/yr)		Coupon wt. loss (mils/yr)		Concentration ratio	Ryznar Index	
	Copper	Carbon steel	Copper	Carbon steel		Water temp. basis	Metal temp. basis
08/04-08/31	0.028-0.190	5.8-8.8	0.21	2.11	1.8-2.7	5.25	4.11
09/01-09/30		5.0-7.7	0.77	0.77	4.2-5.1	4.91	4.07
10/01-10/31		4.6-6.2	1.11	1.11	3.8-4.5	5.25	4.48
11/01-11/30		2.5-5.0	1.34	1.34	4.4-4.9	5.57	4.49

One form of corrosion that appeared to be absent from the ozone treated system was underdeposit corrosion. There were no biological deposits to cause that form of pitting, and no mineral deposits were observed on the coupons or on the condenser tubes. The Scalometer™ test surfaces repeatedly were scaled over during the study, but because of their stainless steel construction, they showed no evidence of pitting. In conclusion, it has been shown that the stand-alone ozone treatment produced acceptable corrosion rates, although the copper-corrosion rates were at the upper end of the acceptable range.

Special Investigations

A wide variety of special investigations was conducted during the ozone treatment evaluation study. The purpose of these investigations was to document any beneficial or nonbeneficial aspects of ozone treatment on a full-scale plant cooling system. The following list shows the special investigations in the order that they will be discussed:

- determination of condenser performance,
- determination of cooling tower performance, and
- determination of "critical scale temperature".

The results of these special investigations, combined with the results of the routine investigations, made it possible to draw many useful conclusions about the effectiveness of ozone as a stand-alone treatment.

Determination of Condenser Performance

In addition to the daily monitoring of flows, temperatures, and pressures around the 1,000-ton chiller condenser, three exhaustive performance tests were conducted. These tests used the Wilson Plot Technique described in the *ASHRAE Handbook: 1983 Equipment Volume* (14). During each test, the condenser was operated at constant heat load and a wide range of water flow rates to produce a matrix of data points of heat transfer coefficient vs water side velocity. By expressing the coefficient and the velocity values in their reciprocal forms and plotting the coordinate pairs, Wilson Plots were created for each condenser test. By extrapolating the lines to zero on the reciprocal velocity scale (infinite velocity), the fluid side resistance theoretically becomes zero. Any change in the intersection point of the plot with the vertical axis is indicative of a change in the fouling resistance on either side of the tubes. Since the refrigerant side conditions were virtually unchanged from one test to the next, any change in the intersection point with the vertical axis of the plot could only be attributed to fouling on the cooling water side of the condenser.

Figure 5 shows the results of the three condenser tests. Although the slopes of the plots varied, the intersection points with the y-axis did not change appreciably. The conclusion supported by these data is that no significant fouling occurred in the condenser tubes during the four months spanned by the test intervals.

This conclusion was verified by two other methods, the first of which was performed concurrently with the condenser-performance tests. A plot of pressure drop on the water side of the condenser vs velocity was constructed from the DP and water-flow data collected during the three special performance tests. Figure 6 shows a plot of these data. The line shown on the graph was plotted from the data collected before ozone treatment was started. The points are from the October and November follow-up tests. Because the line still represents a best fit for the plotted points, no detectable change in condenser pressure drop occurred during the period of ozone treatment.

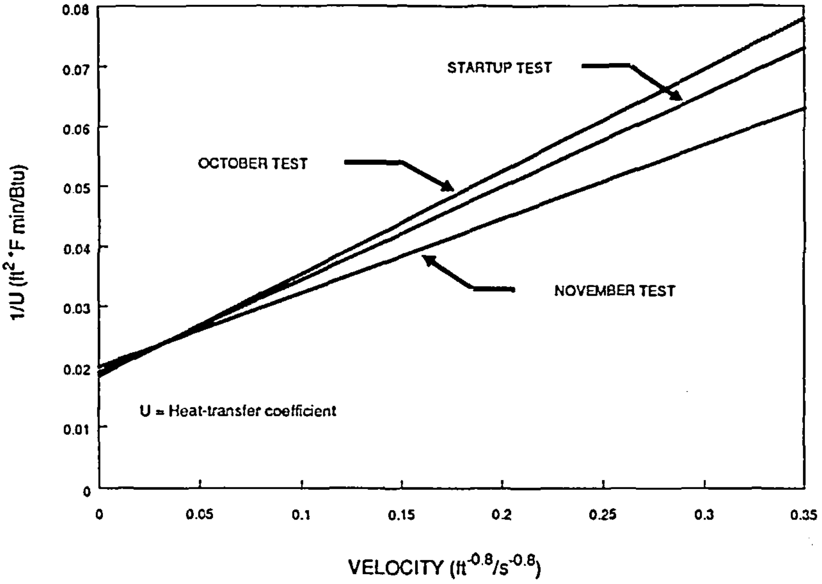

Figure 5. Overall heat transfer resistance.

The last method of confirmation was the visual inspection of the condenser. The condenser that had been monitored and tested throughout the ozone evaluation study was opened for inspection in early December, after 4 months of treatment with nothing but ozone. The tubes and tube sheet of the condenser were free of any detectable deposits. The surfaces of the tubes did not exhibit the slippery biological film that so often is found on condenser tubes.

Determination of Cooling Tower Performance

It was anticipated at the beginning of the study that stand-alone ozone treatment might lead to some fouling in the cooling tower that could adversely affect the thermal performance of the tower. To quantify the impact of any cooling tower fouling, thermal tests were conducted in accordance with Test Code ATC 105 of the Cooling Tower Institute.

A baseline test was conducted in mid-August 1987, and a follow-up test was conducted in late September. By the time of the September test, the crossflow film fill in the test cells had become encrusted with calcium carbonate crystals at the leading edges and on the general surfaces extending back at least 1 ft (30.5 cm) into the fill. This fouling was expected to manifest itself in the form of reduced thermal capability; however, the test data are inconclusive. The test results showed an apparent drop in thermal capability from 87.6 to 81.5%, but the conditions of the second test did not conform to the test code. The test range and the inlet wet bulb temperature of the second test were both lower than the allowable limits. The only conclusion that can be drawn from the cooling tower thermal investigation is that scale deposits did occur in the film fill tower, which may have an adverse impact on tower performance.

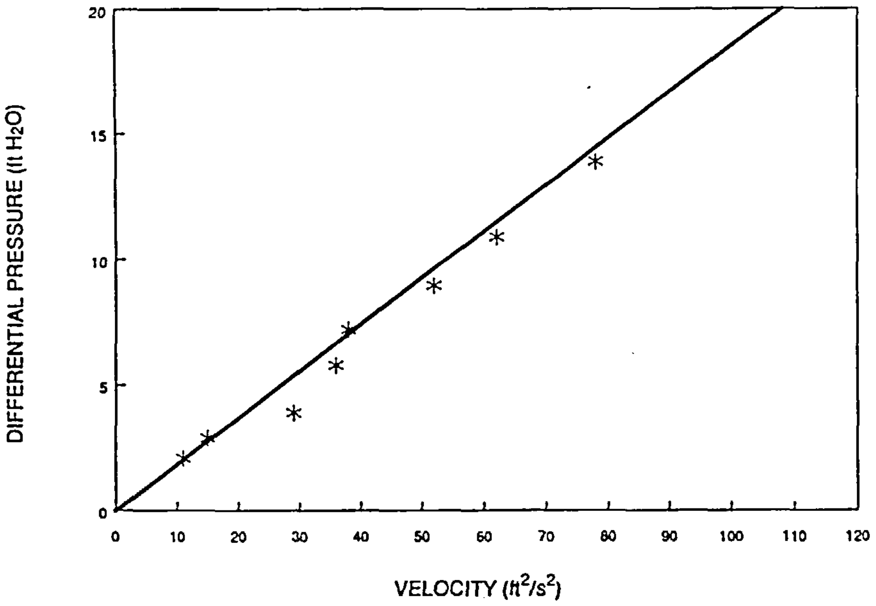

Figure 6. Pressure loss vs tube velocity.

Determination of Critical Scaling Temperature

The Scalometer™ proved to be a very useful tool in the investigation of the tendency toward scale in the ozone treated cooling water system. The original test plan called for continuous operation of the Scalometer™ with a controlled surface temperature of 155°F (68.5°C). This was to simulate the operation of high-temperature tubular heat exchangers that were not represented in the Cooling Tower 9409-2 cooling system. However, 155°F was too high a temperature to afford scale-free operation under stand-alone ozone treatment. The formation of scale at this temperature was immediate and unavoidable. The surface temperature was reduced in 10°F (6°C) increments until a temperature was found at which prolonged scale-free operation was possible. This temperature was designated the critical scaling temperature.

The Scalometer™ operates on a differential temperature principle. Two heating surfaces are exposed to the same hydraulic conditions, with one surface heated (test surface) and the other unheated (reference surface). The heat applied to the test surface is calibrated and controlled to maintain the set surface temperature. It operates in this mode for most of each 4-hr cycle. Then, for the last 15 min of each cycle, both the test and reference surfaces are heated at a lower applied heat flux. The temperatures of each surface are measured and recorded as T (the test surface temperature) and R (the reference surface temperature). The quantity (T-R) is the differential temperature that is indicative of the comparative cleanliness of the two surfaces (7). If a fouling layer exists on the water side of the test surface, its temperature will be higher than the reference surface because of the insulating effect of the deposit. Also, the magnitude of the temperature difference is proportional to the thickness of the deposit. By tracking T-R with time at a constant heat input, the rate of scaling can be determined.

The Scalometer™ was employed as described to determine the critical scaling temperature of the ozone treatment scheme. This parameter was defined as the surface temperature at which the scaling rate equaled the scaling rate measured before the change to ozone treatment. Table 6 shows the Scalometer™ results compared with the average concentration ratio and the average Ryznar index that prevailed during each test run. The scaling rate during the baseline data collection period, prior to the switch to ozone, was 0.86°F/d (0.48°C/d), T-R. A review of the data shows that the scaling rate dropped to the baseline value or lower whenever the surface temperature was controlled to a temperature of 130°F (54°C) or lower. Also, the surface temperature of 135°F (57°C) was a borderline condition with only a slightly increased scaling rate compared to the baseline rate. It was concluded that heat-exchange surfaces in the cooling water systems at the Y-12 Plant below 135°F could be expected to stay free of mineral scale if the concentration ratio is held to 5.0 or lower.

The phenomenon of critical scaling temperature may explain why stand-alone ozone treatment has appeared successful in previous air-conditioning cooling tower applications (3-5), but appeared to fail in applications where heated surface temperatures were higher (15). There are no heat-exchanger temperatures in a vapor-compression chiller over the range of 110 to 120°F (43 to 49°C). At the Y-12 Plant, this phenomenon may be useful in determining which cooling systems would be candidates for installation of ozone treatment facilities.

Summary And Conclusions

The following conclusions are justified by the results of this full-scale evaluation of ozone as a stand-alone treatment for industrial cooling water systems. These conclusions are specific to the makeup water and equipment of the Y-12 Plant; however, they provide information on the application of ozone that may be useful to other investigators.

1. Continuous ozone injection provides excellent control of microbiological fouling organisms in cooling water systems.

2. Stand-alone ozone treatment of cooling water is characterized by enhanced precipitation of calcium carbonate. The location of precipitation sites in a cooling water system varies with design. Sites that showed no tendency toward accumulation of calcium carbonate precipitates were :

   a. the smooth, low-temperature tube surfaces in the vapor-compression chillers and

   b. the splash fill of the cooling tower.

   The following preferential precipitation sites were demonstrated at the Y-12 Plant:

Table 6. Scalometer Test results

Time period (07/87–01/88)	Temperature conditions Degrees F (degrees C)		Average Ryznar Index		Average concentration ratio	T-R rate of increase [°F/d(°C/d)]		Operational conditions: ozone output (%)
	Water	Metal	Water basis	Metal basis		°F	°C	
07/29–07/30	86 (30)	155 (68.5)	5.57	4.45	1.85	0.86	0.48	0[a]
08/04–08/11	86 (30)	155 (68.5)	5.67	4.53	1.90	0.22–0.74	0.12–0.41	100
08/25–08/31	86 (30)	155 (68.5)	4.82	3.69	3.20	2.75–7.51	1.53–4.17	100
09/01–09/04	80 (27)	145 (63)	4.79	3.69	3.70	5.96–8.80	3.31–4.89	100
09/04–09/09	80 (27)	135 (57)	4.95	4.40	4.17	1.94	1.08	100
09/11–09/18	70 (21)	125 (57)	5.00	4.12	5.13	0.38	0.21	100
10/04–10/10	70 (21)	130 (54)	5.13	4.62	3.99	0.49	0.27	100
10/11–10/15	70 (21)	130 (54)	5.30	4.30	3.82	0.54	0.30	75
10/16–10/22	70 (21)	130 (54)	5.31	4.37	4.35	0.74–1.10	0.41–0.61	75
11/03–11/10	65 (18)	130 (54)	5.57	4.49	4.49	1.19–3.10	0.66–1.72	104
12/14–01/03	60 (16)	135 (57)				0.36–3.11	0.20–1.73	104[b]
01/05–01/13	55 (13)	140 (60)				0.13–4.84	0.07–2.69	104[b]
01/13–01/20	55 (13)	140 (60)				2.47–38.34	1.37–21.30	104[b]

[a]Baseline.

[b]Indicates the concurrent use of ozone and chemical inhibitors.

a. the film fill of film-type cooling towers,

b. the rough surfaces of carbon steel pipes and tubes, and

c. the tube surfaces of high-temperature heat exchangers.

These conclusions can be used as application criteria for ozone treatment in specific cooling systems.

3. The corrosion rates recorded during the Y-12 Plant study were typical of good corrosion control under alkaline treatment conditions. The absence of any detectable biological foulants makes it improbable that any biological pitting attack would occur in an ozone treated system.

4. The Scalometer™ results revealed a plausible explanation for the differing results that have been previously reported in the technical literature. The Y-12 Plant study showed that a critical scaling temperature exists, which is significantly higher than the condenser tube surface temperatures in a vapor-compression chiller. Cooling tower operators who are considering ozone as a stand-alone treatment should first determine the critical scaling temperature for their specific makeup water at the concentration ratios that are planned for their operation.

5. The combination of a redox-potential instrument on the cooling water inlet to the heat exchangers and an ultraviolet light ozone analyzer on the ozone generator outlet provide an effective means of remote on-line problem diagnosis for the ozone delivery system.

6. Because of the uncontrollable losses of cooling water from the Cooling Tower 9409-2 system, it was not possible to investigate the ozonation of a cooling system operating at very high concentration ratios. Further research is needed, using some of the same investigative methods as were used in this study.

7. At the Y-12 Plant, only 12% of the ozone generated produced a free unreacted residual of ozone in the cooling water. Multipliers of 8:1 or higher may be needed in the sizing of ozone delivery systems for clean water cooling systems. Systems that have high loads of organic materials, manganese, or iron may require much greater sizing factors. Pilot testing is needed at each site before economical generator/contactor sizing can be performed.

Further Ozone Investigations

The Y-12 Plant has placed a 3-year contract with Southern University, Baton Rouge, Louisiana, to investigate further areas that were inconclusive in this study. Southern University has installed the ozonation system on one of its cooling towers on campus and has begun work in the following areas:

- determine if 135°F (57°C) is the critical scaling temperature for different makeup waters,

- determine if the critical scaling temperature can be increased artificially by the addition of chemicals,
- determine if the critical scaling temperature moves up or down as concentration ratio increases,
- assess materials of construction compatibility with ozone,
- investigate scale-forming mechanisms of ozonated water,
- optimize the total system design for an ozone treated cooling tower, and develop a computer-simulation program for ozonated cooling tower system.

The 3-year study is not limited to the above areas, but they are a starting focal point for the study. As results from the aforementioned areas of study are compiled, future reports may be provided at other cooling tower symposia and publications.

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Key Words

Ozone, Cooling Water Treatment, Cooling Tower Water Treatment, Air Conditioning Cooling Towers, Microbiological Control, Corrosion Control, Critical Scaling Temperature

Résumé

Cette publication constitue le premier compte-rendu technique ayant trait à l'évaluation en continue d'un traitement à l'ozone de l'eau d'une tour de réfrigération. Les données présentées illustrent les résultats d'un tel traitement dans un système de réfrigération d'air conditioné de 3400 tonnes équipant l'installation Y-12 de Oak Ridge, Tennessee. L'installation est exploitée par "Martin Marietta Energy Systems, Inc." pour le Département de l'Energie des USA. Les données de transfert de chaleur et l'inspection des équipements confirment qu'il existe une température limite en dessous de laquelle il ne se produit aucuns dépôts minéraux sur les surfaces d'échanges de chaleur. Si la température de ces dites surfaces dépasse le seuil limite, on constate la formation de couches de carbonate de calcium. Cet effet de température limite pourrait expliquer pour quelles raisons le traitement à l'ozone est d'une part propagé comme procédé favorable pour les tours de réfrigération d'air conditionné, et que d'autre part il s'est avéré inapte pour les processus de réfrigération à haute température. Des plans concernant de futures recherches en matière d'ozone sont également discutés.

Zusammenfassung

Diese Veröffentlichung ist der erste technische Statusbericht einer laufenden Erprobung der Ozonbehandlung eines Kühlturmwassers. Es werden Daten vorgestellt, die die Ergebnisse einer Ozonbehandlung in einem 3400 t Kühlsystem einer Klimaanlage illustieren, bei der Oak Ridge Y-12 Plant, Oak Ridge, Tennessee. Die Anlage wird betrieben von Martin Marietta Energy Systems, Inc., für das US-Department of Energy. Wärmeübertragungsdaten und die Materialbeobachtung bestätigen, dass ein Temperaturgrenzwert besteht unterhalb dessen die Wärmeaustauschoberflächen frei bleiben von mineralischen Ablagerungen. Wärmeaustauschoberflächen die den Temperaturgrenzwert überschreiten weisen eine Kalziumkarbonatausfällung auf. Der Temperaturgrenzwerteffekt könnte erklären, warum die Ozonbehandlung als ein erfolgreiches Verfahren von Kühltürmen in Klimaanlagen beschrieben wird, sie sich jedoch als nicht erfolgreich erwiesen hat in Hochtemperaturkühlverfahren. Pläne für zukünftige Ozonuntersuchungen werden diskutiert.